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THE SPACE GROUPS OF CRYSTALS OF β-CHLORONAPHTHALENE AT DIFFERENT TEMPERATURES

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Plates 1A & 1B

ABSTRACT. The Debye-Scherrer patterns of crystals of β-chloronaphthalene at 30°C and −180°C have been studied and analysed. As it was not possible to interpret the patterns satisfactorily single crystal rotation photographs about *a*-axis and another zone axis have been taken. The unit cell has been found to be different from that reported by Neuhaus. The dimensions of the unit cell observed are $a = 7.48$ A, $b = 17.92$ A, $c = 6.35$ A and $\beta = 97°15'$, and there are 4 molecules in the unit cell. The density calculated is 1.270 which agrees with the observed value 1.266. The space group is $P2_1/m$ or C^2_{2h}.

At −180°C the space group remains the same as at 30°C, but the *a*-and *c*-edges of the unit cell contract while the length along *b*-axis remains almost unchanged. The dimensions of the unit cell at −180°C are $a = 7.28$ A, $b = 17.88$ A, $c = 6.17$ A and $\beta = 98°53'$.

INTRODUCTION

The Debye-Scherrer pattern of the crystals of β-chloronaphthalene was studied earlier by Neuhaus (1939) and he found the crystal to be monoclinic, the dimensions of the unit cell being $a = 7.65$A, $b = 5.93$A, $c = 18.4$A and $\beta = 103°$. The density calculated on the basis of four molecules per unit cell was found to be 1.36, but the actual measurement gives the value 1.266 for the density at 16°C. Hence there seemed to be some discrepancy between these two values of the density. Also, the cell dimensions reported by Neuhaus does not account for satisfactorily all the spacings observed by him. It was, therefore, thought worthwhile to re-investigate the structure of the crystal. In this attempt, besides photographing the Debye-Scherrer patterns of the crystal at 30°C and −180°C, single crystal rotation photographs have also been taken by rotating the crystal about different axes. The results obtained in this case indicated that the cell dimensions are different from those reported by Neuhaus. These results are reported in the present paper.

EXPERIMENTAL

The compound β-chloronaphthalene was procured from an old stock supplied by Dr. Frenkel and Dr. Land of Germany. It was recrystallised from

solutions in benzene. The Debye-Scherrer patterns due to the crystals at about 30°C and also at the temperature of liquid oxygen were photographed using a camera used previously by Krishnamurti (1956). The diameter of the camera was determined by studying with it the Debye-Scherrer pattern due to aluminium powder and was found to be 8.72 cm. Although the substance is solid at the room temperature it was sealed in a Lindemann glass capillary tube to prevent rapid sublimation. A Seifert X-ray tube running at 32 K.V., 20 mA was used to photograph the patterns.

The crystals were in the form of flakes and in order to study single crystal rotation photographs such a crystal was sealed in a Lindemann glass capillary tube and the plane faces of the flake were made vertical by mounting the tube on a goniometer head. After several trials with different axes of rotation a photograph showing layer lines was obtained. The trial was continued with different axes in the plane of the large face of the flake. Altogether four photographs showing layer lines were obtained in this way

RESULTS AND DISCUSSION

The Debye-Scherrer patterns and two of the rotation photographs are reproduced in Figs. 1, 2, and 3 and 4, Plates IA and IB. The spacings calculated from Debye-Scherrer rings are given in Tables I and II It can be seen that a reflection corresponding to a spacing 8.96A occurs in the zero layer line in both the rotation photographs. As the axes of rotation lie in the plane face of the flake this spacing corresponds to that of the planes parallel to the large face of the crystal. Further, there are some reflections in Fig. 3 along two straight lines passing through the central spot and making an angle 7°15′ with the zero layer line. Hence it is assumed that the a-axis is vertical in this case and the angle β is 97°15′ and that the spacing mentioned above is due to planes normal to the b-axis This spacing was taken as that due to 020 reflection. The primitive translation along a-axis derived from Fig. 2 is 7.48A. The c-axis could not be located and no rotation photographs about the c-axis could be taken. Table I, however, shows a strong reflection corresponding to a spacing 3.175A. Tentatively, this was assumed to be 002 reflection and the following cell dimensions were assumed for the crystal at 30°C.

$$a = 7.48 \text{ A}$$
$$b = 17.92 \text{ A} \qquad \beta = 97°15'$$
$$c = 6.35 \text{ A}$$

This gives four molecules per unit cell with the density 1.270, which agrees with the observed value 1.266 (Cook & Jones, 1953).

The spacings of the planes giving reflections in the rotation photographs were then determined from the position of the spots using the relation $\cos 2\theta = \cos\phi \cos\mu$, where θ is the Bragg angle, μ is the angle of elevation of the reflected

Fig 1

Fig 2

Fig 3

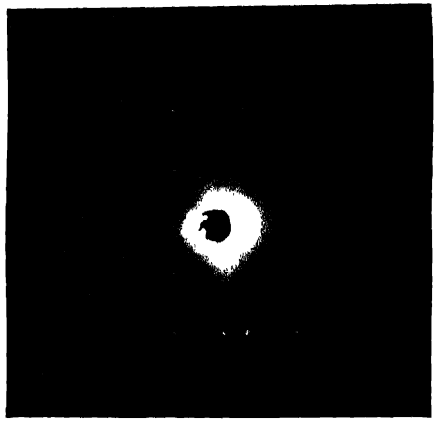

Fig 1 Debye-Scherrer pattern of β–chloronaphthalene at 30 C
Fig. 2 Debye-Scherrer pattern of β–chloronaphthalene at –180 C.
Fig 3. Single crystal rotation photograph of β–chloronaphthalene about *a*-axis.

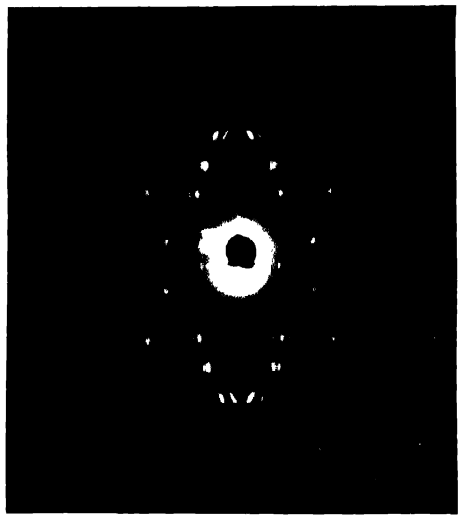

Fig. 4 Single crystal rotation photograph about a zone axis of β–chloronaphthalene

ray above the equatorial plane and ϕ is the angle made by the direct ray with the projection of the reflected ray in the equatorial plane. The probable spacings of the different planes of the crystal having the cell dimensions given above were also calculated. These are given in Table III.

TABLE I

Spacings of β-chloronaphthelene at 30°C from Debye-Scherrer photograph

Sr. No.	Visual Intensity	Sin θ	Spacings observed by Neuhaus in A.U.	Observed spacings in A.U.	Calculated spacings in A U.	Indices
1	vs	0860	8.95	8.96	8.96	020
2	vs	1664	4.63	4 63	4.65	130
3	m	1758	4 44	4 38	4 39	111
4	vs	2075	3 76	3 716	3 71	200
5	vs	2425	3.17	3 175	3.175	002
6	w	.2619	2.96	2 95	2.95	$15\bar{1}$, $23\bar{1}$
7	w	2802	2 76	2 748	2 74	112
8	w	3307	2.33	2.328	2.32	152
9	vw	.3616		2.129	2.13	162
10	m	3991	1 93	1 929	1.93	103
11	m	.4221	1 82	1 83	1.837	302

TABLE II

Spacings of β-chloronaphthalene at −180°C

Sin θ and Intensity	Spacings observed d in A U	Spacing calculated d in A.U.	Indices
.0861 vs	8 943	8 94	020
.1678 vs	4.59	4.59	130
.1824 m	4.22	4 217	111
.2139 vs	3.60	3.60	200
.2525 vs	3.049	3 049	002
.2646 w	2.91	2.919	$15\bar{1}$
.2905 w	2.65	2.64	112
.3374 w	2.288	2.289	152
.3669 vw	2.10	2 104	162
.4158 w	1.91	1.90	103

TABLE III

Spacings of β-chloronaphthalene

Sr. No.	Indices	Spacings in A.U. calculated	Spacings in A.U. observed	Figure Number in which observed
1	020	8.96	8 96	1,3 and 4
2	130	4 65	4 63	1 and 4
3	101	4 53	4 535	3
4	040	4.48	4.47	3 and 4
5	$12\bar{1}$	4.45	4 46	4
6	111	4.30	4 38	3
7	200	3.71	3.71	1 and 3
8	220	3 428	3.42	1
9	211	3 33	3.33	3 and 4
10	002	3 175	3.175	1
11	221	3 14	3.13	3 and 4
12	201	3 07	3 08	4
13	$10\bar{2}$	3.04	3.03	4
14	231	2 95	2 95	1 and 4
	$15\bar{1}$	2 94	2.93	1
15	112	2.74	2.75	1 and 4
16	$24\bar{1}$	2.70	2 70	4
17	122	2 65	2.66	3
18	152	2 32	2 328	1 and 4
19	$32\bar{1}$	2.317	2.317	3
20	$16\bar{2}$	2 13	2 13	1
21	103	1.94	1 93	1 and 4
22	322	1.908	1 903	3
23	172	1.880	1 885	4
24	302	1.837	1 83	1
25	202	1 804	1 803	4

It can be seen from Table III that there is no restriction for the general planes of indices *hkl* and *hol*, but no reflection from planes of indices *oko* with odd values of *k* has been observed. Hence the space group is $P2_{1/m}$ or C^2_{2h}.

The Crystal at −180°C.

It can be seen from a comparison of Tables I and II that almost all the reflections observed in the Debye-Scherrer pattern of the crystal at 30°C persist when the crystal is cooled to −180°C, but the spacings diminish a little. The primitive translation along *b*-axis, however, remains almost unchanged when the crystal is cooled to −180°C, although the *a*-axis and the *c*-axis contract to a large extent at the low temperature. The dimensions of the unit cell at −180°C are: $a = 7.28$A, $b = 17.88$A, $c = 6.17$A and $\beta = 98°53'$.

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